

The University of Chicago

STIEGLITZ THEORY OF COLOR
PRODUCTION

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1937

By

ROBERT MacFARLAN COLE

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INTRODUCTION

For half a century or more with each advance in physics, particularly atomic physics, there have appeared new explanations or theories attempting to elucidate the fundamental mechanism of color production. All of these theories of the past have been found faulty when subjected to the test of fulfillment of conditions imposed as new data have come to light. In 1923, the Stieglitz theory of color was published¹—which unlike the older theories of Baly, Campbell, Witt, and others, showed very good conformity with the requirements of modern atomic concepts. Using the Lewis-Kossel or the Bohr interpretations of the Rutherford type of atom model in which any molecular substance depends for its existence on the maintenance of a joint electronic orbit by two atoms, this theory similarly explains color production in terms of electronic functions and in harmony with the postulates of the latter theories. Not only is it possible to explain in terms of electronic properties the bonds between two atoms in a molecule, but also the production of color may be explained in terms of electronic properties. Thus, an electronic orbit jointly maintained by two atoms within a molecule may serve as the locus of light absorption and emission; the emitted frequency (color of the substance) consists of the remaining or unabsorbed frequencies of the incident white light. In other fields definite pieces of research have been carried out with the view to test this theory further as to conformity with various data and the results thus far have been in accord with the claims of the theory.

The salient feature of this theory is the concept of two atoms, usually carbon atoms, closely situated and usually adjacent or alternate, in a molecule both of which exert an attraction for the same electrons, or pair of electrons, which they likewise jointly maintain. The more positive atom of the two may exert sufficient attraction to loosen greatly the restraining action of the other less positive carbon atom and so cause a marked

¹Proc. Nat. Academy of Sci., 9, 303 (1923).

displacement of the electron or electrons such that they oscillate in an intermediate position between the two atoms. In this state the electrons are highly sensitive to the slightest change of light energy of visible frequencies. When light falls on such a system, some of the frequencies are absorbed in such a manner as to increase the electrons' orbital diameters with respect to one of the atoms; somewhere in their displacement they reach a critical frequency at which they become both absorbers and emitters as their orbital diameters are raised and lowered alternately.

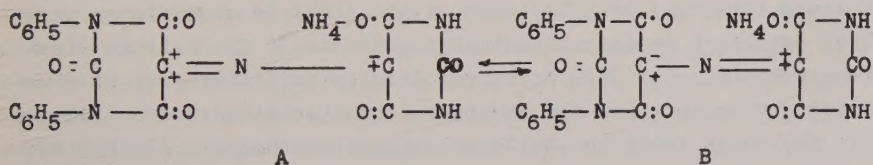
As evidence for the assumption of two such atoms as those above mentioned are the data establishing the fact that every dye-stuff, without exception, possesses both an oxidizing or color-producing group (chromophore) and a reducing or color-enhancing group (auxichrome). It is also recognized that an oxidizing group possesses an incomplete complement of electrons, that is, it possesses a positive character; likewise, a reducing group carries loosely held electrons which it tends to give up, representing a negative potential. It is this pair of opposing electrical characteristics manifested by the two atoms that is of just sufficient difference in restraint and attraction to hold in equilibrium the planetary electron or electrons which they jointly maintain, and that constitutes a light-absorbing and emitting doublet. The reason two carbon atoms, rather than atoms of another elemental type commonly fulfill the role allotted above, is again due to evidence accumulated and accepted that carbon possesses to a greater degree than other elements the property of becoming partially or wholly positive or negative in character. As is well known, carbon stands between the metals with their tendency to become electropositive, and the non-metals with their tendency to become electronegative. It shares both of these tendencies and they are better balanced in carbon than in any other element.

Quinones are colored—yellow, orange, red, as a rule. The source of these colors is to be found in the loosening effect of the strong oxidizing atoms (the two C atoms of the $C::O$ groups) on valence electrons within the quinone group itself. Presumably the electrons which are thus freed from interatomic restraints sufficiently to absorb visible light are electrons of the two ethylene groups. Ethylene groups are rather easily oxidized, which proves that the electrons of the second bond are easily affected. In quinones, moreover, the ethylene groups are found in

a conjugated bond system, in which the valences are particularly active. In dyes these effects of the oxidizing quinoid groups (the chromophores) on the electrons of neighboring atoms within the chromophores are obviously not lost and evidently they must form supplementary sources of light absorption and therefore of color. Their colors, as indicated above, are rather shallow ones; they contribute, no doubt, to the well-known formation of absorption bands in the spectrographic analysis of the color. But it is the electro-chromophoric group resulting from the combination of strong oxidizing groups (chromophores) with strong reducing groups (containing the auxichromes) as found in dyes, which yield the deeper and more intense, colors characteristic of the dyes.

Among other dyestuff types that have served as very fruitful sources of evidence in favor of this theory are the murexides. When these dyestuffs are of the symmetrical type, the molecule is practically divided into two equal halves held together by a nitrogen bridge. These two half-molecules would be architecturally identical if it were not for a discrepancy in their electronic quota; a shortage of one electronic pair to complete the quota for each, sets up a condition as described above and shown graphically below in which one of the half-molecules is the oxidized and one the reduced form of the other. Inasmuch as the problem of this paper concerns itself with the two isomeric, possibly tautomeric, forms of the unsymmetrical diphenylmurexide a list containing some of the points of requirement of the theory in conformity with the experimental evidence for this specific substance is given below.

Stieglitz Color Theory



Asym. Diphenylmurexide

1. Atoms would have to migrate or move if electrons do what is required of them in the older theories. Any vibration within the molecule of a dye to produce color must be of the order

of the vibration of light since a part of the white light is absorbed and the complementary color is seen.

2. If the production of color is due to the actual passage to and fro of electrons from the reducing carbon atom ($C\bar{+}$) to the oxidizing atom ($C\bar{+}$) in the molecule of a dye, such as murexide, then the structural changes involving atoms and groups of atoms which would attend such passages of valence electrons would have to occur reversibly with a speed approximating that of light.* Hence, if color is produced without the motion of said groups, it must be due to electrons, non-migratory, but still sufficiently free of inter-atomic restraint to set up a light-absorbing doublet.

3. If the electrons actually migrate when color is produced in murexide (during formation of latter) then the nitrogen bonding would so change in its relationship to the almost identical rings to which it is attached that on acid hydrolysis it would be left attached to the opposite ring from that on which it was originally. Thus, if the initial components of the murexide were diphenyl uramil and alloxan, then after hydrolysis, uramil and diphenyl alloxan would remain. However, if the close proximity of the oxidizing carbon atom ($C\bar{+}$) to the reducing atom ($C\bar{+}$) frees the pair of electrons, represented by the sign (-) in ($C\bar{+}$) from intra-atomic restraints sufficiently to absorb light by their own vibrations, the color would be produced without the structural changes described in (1) and (2).

4. Such a source of color, without completion of any actual migration to and fro of electrons in the production of color, does not preclude the probability that side by side with the absorption of light and production of color by the vibration of the loosened electrons of ($C\bar{+}$), there might occur in much slower parallel reactions occasional actual migrations of the valence electrons from ($C\bar{+}$) to ($C\bar{+}$), an intramolecular oxidation-reduction reaction, bringing about the structural changes discussed in (1) and (2); but these would be incidental changes, common to all systems

*The structural changes in an ordinary dye, say of the quinoid type, would be even more complex than those of a murexide. For instance, they would involve reversible changes from quinoid to benzoid nuclei.

The signs + and - indicate partial polarity rather than ionic polarity. Thus, $C\bar{+}-N$ represents the same relation as $C :: N$, and $C-C\bar{+}-N$, the same as $C : C : N$.

in which oxidizing and reducing components are in closest proximity, but would have nothing to do with the color production.

5. If the electrons actually migrate to and fro, when color is produced in the case of, say, unsymmetrical diphenylmurexide, we would have structural changes represented by structures "A" and "B" as indicated above. On hydrolysis "A" would give diphenylalloxan and uramil, while "B" would give alloxan and diphenyluramil. The system would have to reach the equilibrium point for the two forms with the speed approximating that of light.

6. Consequently, if it can be shown that an unsymmetrical diphenylmurexide prepared from diphenylalloxan and uramil gives these same products as hydrolysis, and that an isomeric unsymmetrical diphenylmurexide prepared from alloxan and diphenyluramil gives by hydrolysis these original components again, the Stieglitz view would be substantiated. In other words, the establishment of the fact that there are two isomeric diphenylmurexides which exist at least for a measurable length of time, would substantiate the Stieglitz theory. That in the course of time "A" should form some of "B" and "B" some "A" reversibly by ordinary intramolecular oxidation and reduction is to be expected, especially in solution and its attendant free ionization. The two substances would thus be tautomers of the oxidation-reduction type. The studies of Kurt Meyer and of Knorr on acetoacetic ester have shown that tautomeric changes are extremely sensitive to catalysts such as acids and bases and under such conditions take place very rapidly. But in the absence of such catalysts the changes are very slow; the complete cycle keto-enol for the pure tautomers requires seventeen days according to Meyer and half a year according to Knorr.

It is evident from these considerations that speed in the preparation and analysis of tautomeric murexides is a favorable factor. It is also evident that the isolation and proof of existence of a very few pairs of such tautomers would bring the essential proof of the Stieglitz theory. In other instances the equilibrium expressed above might well be reached so fast that a separation of the tautomers is rendered impossible. As is well known, this is exactly the situation for tautomers in general; of the thousands of pairs of tautomeric substances, only a very few pairs have actually been separated and the individual tautomers identified.

7. Summing up, if it can be shown that in diphenylmu-

reoxide the two phenyl groups remain in the original (alloxan or uramil) nucleus from which the dye was prepared, then the existence of two tautomeric forms is proved and the Stieglitz theory substantiated. Thus, diphenylalloxan and uramil should give a diphenylmurexide, from which by hydrolysis diphenyalloxan and uramil should be recovered in preponderant quantities, while from alloxan and diphenyluramil a second diphenylmurexide should be obtained which on hydrolysis would yield alloxan and diphenylmuramil in preponderant quantities.

8. For the identification of such tautomeric dyes a study of their absorption bands held out the possibility of identification by optical means.

EXPERIMENTAL PART, I

Apparatus.—The principle of the equipment used for this work is based on the fact that light from a suitable source falling on two achromatic deviating prisms will produce two axially parallel pencils, which pass through a pair of absorption tubes containing the solutions and thence on to the photometer through two windows contained in the photometer and back of which are two square-ended polarizing prisms. After passing through these, the pencils later combine to two almost completely juxtaposed fields by means of a large prism. The combined pencil now passes through a condenser which can be so adjusted on the barrel of the photometer as to produce correct conditions of illumination while the object glass further along at the eye-end focuses the image of the dividing line through the fields onto the spectroscope slit. These two light fields, or pencils, can be varied in relative intensity by a third polarizing Nicol which is mounted on the circular divided head on the photometer. The relationship holding between these pencils is:

$$\frac{I_0}{I} = \tan^2 \theta$$

where I_0	=	intensity of light incident on first Nicol
I	=	intensity of light incident on second Nicol
and θ	=	angle through which large Nicol must be turned in order that both fields may be brought to the same intensity.

In other words, the solution which is of a definite concentration

and is contained in one of the cells, possesses a definite absorption value.

Now, if the Nicol prism controlling the solvent cell be rotated through such an angle that the light intensity passing through has been reduced to exact equality with the light intensity from the cell containing the solution in question, then from the above determination it is seen that it is necessary only to find what that angle is. Inasmuch as this angle can be read off directly on the head of the photometer scale, the square of the tangent of this angle can be taken from the table. After passing through the photometer, this two-field pencil of light is next admitted through the spectroscope slit at the collimator, the jaws of which are adjusted to an aperture corresponding to one revolution of the milled head. Any region of the absorption band can now be read off directly on the wave-length scale. The readings thus taken, consisting of wave-length, extinction angle, and concentration of the solution are tabulated below for each individual substance.

EXPERIMENTAL PART, II

In the ultra-violet in conjunction with the Quartz Spectrograph, the Wedge-Sector is used in place of the photometer; a Hilger-Nutting photometer was used in the visible region. The source is a tungsten arc under water operated by means of a Tesla Coil under an E. M. F. of about a million volts. The light passes out of the arc-bulb through a quartz window and thence through two cells (quartz windows) each screwed in front of a moving sector one of variable aperture and both set at such an angle as to throw equal illumination into each cell. The light emerging from the cells is then passed through the collimating slit of the Spectrograph and to the photographic plate. In the sector of variable aperture is placed the cell containing the solvent and in the sector of fixed opening is placed the solution. The opening in the sector is adjustable in angles such that the openings follow a logarithmic curve gradually extinguishing the light passing through the solvent in terms of the tangent law given for the Nutting Photometer where the Nicol prism for the solvent-cell is rotated until extinction is reached. Although no wave-length positions are read off, they are recorded on the plate which covers the entire ultra-violet and the head of the absorption band is recorded by the

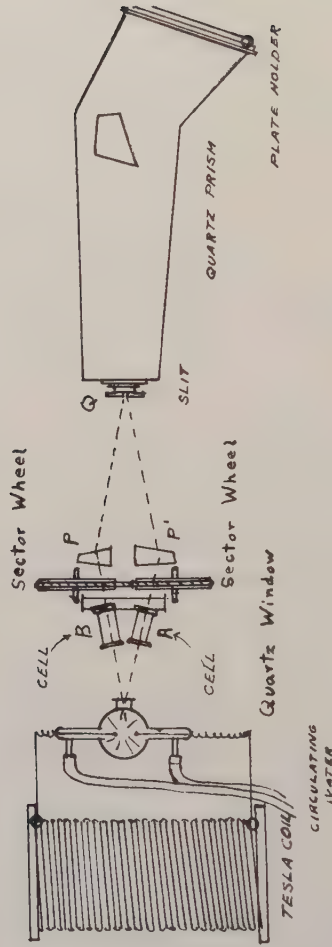


Fig. 1

above variation in the sector setting. Also, instead of varying the cell-length or the concentration as was done in the visible, the times of exposure were varied as given in the table. In other words, each setting gives an absorption band showing the extinction point where the light getting through the solvent has been let down to that of the solution. Summation of these in a series shows the head of the band.

SLIT OPENING OF TWENTY DIVISIONS OF ONE TURN

Number	Sector Open	Plate Holder	Time Seconds
1.	0	10	Blank 20 Scale 7
2.	0	15	13
3.	.1	20	20
4.	.2	25	25
5.	.3	30	32
6.	.4	35	40
7.	.5	40	50
8.	.6	45	63
9.	.7	50	79
10.	.8	55	100
11.	.9	60	159
12.	1.1	65	251
13.	1.3	70	316
14.	1.4	75	10 minutes
15.		80	Blank 20 Scale 7

Solutions of approximately one-tenth of 1 per cent were used throughout.

THEORETICAL

Calculations.—In order to plot the tabulated absorption-spectral data, it is necessary to calculate the extinction coefficients and absorption percentage. This can be done by making use of proportionality relationships existing between intensity and absorption of light at definite concentrations of solution. This absorption, defined as the decrease in intensity per unit of length or of concentration, is also proportional to the original intensity. Expressed mathematically:

$$-\frac{dI}{dC} = kI$$

In this equation, I is the intensity of light after pass-

ing through a layer of C units of concentration. Then

$$-\frac{dI}{I} = k dC$$

By integration between the limits I and I_0 and C and C_0 , the following equation is obtained, where I is the intensity after passing through C units of concentration of absorbing material and I_0 is the intensity of light when $C = C_0$ or zero concentration, thus:

$$-\left[\log_e I\right]_{I_0}^I = k \left[C\right]_{C_0}^C \quad \text{or} \quad k = \frac{-2.303}{C} \left[\log_{10} I_0 - \log_{10} I \right]$$

$$k = \frac{-2.303}{C} \log_{10} \frac{I_0}{I}$$

By the application of this formula to the unit concentrations of the individuals tabulated, an angle was obtained from the graph in each case at the apex of the extinction angle by intersecting the tangents to the normals. Thus, in the case of tetraphenylmurexide where the angle for unit concentration is 74° , the remaining light corresponds to the $\tan^2 16^\circ = .817$. Therefore:

$$k = \frac{2.303}{1} \log_{10} \frac{1.00}{.817} = 2.303 \log_{10} 1.15$$

$$k = 2.303 \times .060 = .138$$

The numerical value of k having thus been established, the intensity at any of the recorded concentrations may be calculated with the aid of this constant k. In each case, in this work, it is seen that the original unit concentration of 10 parts per million (except in the case of alloxan) was successively doubled for the higher concentration. Thus, for example, where 40 parts per million were used, the k value of tetra-phenyl murexide may be substituted as follows:

$$.138 = \frac{2.303}{4} \log_{10} \frac{1.00}{1} = -.576 \log_{10} I$$

$$\text{or} \quad \log_{10} I = -\frac{.138}{.576} = -.239$$

$$\text{therefore:} \quad I = \text{anti-log } 1.76 = .5754$$

Thus, the intensity is reduced 57.54 per cent of its original value after passing through four times the concentration of solution. In order to find the concentration (upper limit) where 95 per cent of the light is absorbed, substitution gives:

$$.138 = \frac{2.303}{C} \log_{10} \frac{1.00}{.05}$$

$$C = 16.6 \log_{10} 20$$

$$C = 21.58 \text{ times unit concentration}$$

PREPARATIVE

Diphenylbarbituric Acid.—After numerous attempts to prepare this substance by the prescribed methods given in the literature for the unsubstituted barbituric acid, it was finally decided that some modification would be necessary if anything like reasonable yields were to be obtained. The apparent weakness of the methods given for the preparation of the unsubstituted murexides from a standpoint of carrying over into the substituted murexides, resides in the choice of solvents and not in the nature of the condensing agents. Such solvents as chloroform, carbon tetrachloride, etc., are admirably suited to the preparation of the unsubstituted substance because the condensation temperature for area and malonic acid falls below their boiling points. In the case of diphenylurea, however, the solubility is not only much too low but the condensation is carried on decidedly above their boiling points. The much weaker basic character of the diphenylurea probably accounts for this higher temperature requirement. In any event, by using chlorobenzene in which diphenylurea is fairly soluble, a smooth-working practicable method was obtained. Also, glacial acetic acid, either as a solvent or condensing agent should be used in minimum amounts.

Weights Used	Theor. Weights	Boil. Pt.
Malonic acid..... 50 grms.	48 grms.	
Diphenylurea.....100 "	106 "	
Acetic anhydride.....100 "	98 "	137° C.
Chlorobenzene.....700 cc.		132° C.

The chlorobenzene and diphenylurea are placed in a one-litre flask and heated over a direct flame until solution is complete. In order to accomplish this the tempera-

ture may be raised to the boiling point of chlorobenzene, if necessary. In a separate flask the malonic acid is dissolved in the minimum amount of glacial acetic acid (hot) necessary for solution. The acetic anhydride is added and the contents of the second flask carefully added to that of the first flask. The reaction mixture is allowed to stand in a warm place for several hours at the end of which time considerable crystallization of the diphenylbarbituric acid has taken place. The flask is then allowed to cool gradually and stand for twenty-four hours when the first crystallization is complete. The contents of the flask are brought on a Buchner filter. The filtrate and the small amount of chlorobenzene wash-liquid are added together, returned to the original flask and again heated for about four hours on the water bath. The flask is again allowed to cool and after standing twenty-four hours will contain a second crop of crystals. The added weights of these two crops of crystals should be equivalent to 83-85% of theoretical. An additional yield may be obtained by further heating and crystallization. The crystals are pure white, monoclinic needles, which collect in star-shaped clusters.

The above procedure can be used for preparing the di-tolyl derivatives which condense slightly easier than the phenyl but in the case of the di-a-naphthyl and di-b-naphthyl derivatives, the solvent is changed to a-chloronaphthalene and the amount is 1200 cc. for the same molar quantity.

Diphenylvioluric Acid.—This product is very easily prepared in a number of ways, either sodium or potassium nitrite and diphenylbarbituric acid being used, as follows:

1. A chlorobenzene solution of diphenylbarbituric acid is shaken (warm) with aqueous nitrite solution.
2. A chlorobenzene solution of diphenylbarbituric acid is ground (trituated warm) with aqueous nitrite solution.
3. A methyl alcohol solution of diphenylbarbituric acid and dry nitrite in methyl alcohol (warm).
4. An ethyl alcohol solution of diphenylbarbituric acid and dry nitrite ground (trituated warm).
5. Ethyl or amyl nitrite and diphenylbarbituric acid refluxed in alcohol.
6. Dry diphenylbarbituric acid shaken in a flask with an aqueous solution of nitrite (warm).

Each of these methods possesses certain advantages and disadvantages. In Number 1, the reaction is more rapid than in Number 2, but separation is more difficult. Number 3 is more rapid and complete than Number 4 but in 3 the excess nitrite is difficult to remove—being soluble in methanol. Number 5 is,

comparatively, too complicated. An advantage of Number 2 is that the product is uncontaminated with the excess of nitrite; it has the disadvantage that the unconverted barbituric is present with the product. In all of these methods it is well to bear in mind that the diphenylvioluric acid is sensitive to hydrolysis and will not keep in water. Number 6 has one distinct advantage over the others in that a pure product can be obtained directly. Considering the rates of nitroso formation and hydrolysis, the optimum time and temperature are approximately three hours and at 50° C. for Number 6. In order to avoid contamination of the product from excess nitrite, the diphenylbarbituric acid is used in excess.

Fifty grams of diphenylbarbuturic acid are placed in a shaking flask with 20 grams of nitrite of soda dissolved in 50 cc. of water. The temperature is raised to 50° and the flask placed in the shaking machine. It is necessary to warm the flask every half hour. After three hours, the nitrite has disappeared and the nitrose solution is filtered from the unchanged barbituric acid. The product can be converted into the free acid or used directly by reduction to the corresponding uramil. The recovered barbituric acid can be used again. The sodium salt may be obtained very pure at this stage by salting-out, extraction of the dry material with ethyl alcohol and crystallization. The yield is theoretical.

Diphenyluramil.—Of the three methods given below for the reduction of diphenylvioluric acid to diphenyluramil, the hydrogen sulphide method has been found much superior to the others for the preparation in practical amounts and is given, herewith:

A saturated solution (100 cc., 6% by weight) of diphenyl sodium violurate are placed in a 200 cc. Ehrlenmyer flask and a stream of hydrogen sulphide passed in. The contents of the flask are protected from oxidation by means of a wad of paper stuffed into the neck of the flask. After a few minutes, the deep purple color changes to white, warms up slightly, and a turbidity of sulphur and a small amount of free violuric acid appear. The acid then begins to dissolve (probably in the acid sodium sulphide) and the reduction commences with the formation of a yellow colored solution. This yellow solution, which is, no doubt, diphenyluramil hydro-sulphide, grows continually stronger and then crystals of the amine, or amine-hydrosulphide begin to separate out. As the process continues, the flask gradually fills with these pearly, scintillating, tiny plates of diphenyluramil or the hydrosulphide until the flask contents becomes a stiff mass at the end of about two hours, depending on the stream of gas used. Considerable care must be exercised from this point on, in the handling in order to avoid oxidation which is manifested by the red coloration, due to tetraphenylmurexide. This is best managed by filtering in an atmosphere of hydrogen or hydrogen sulphide. The washing is

done by means of a small amount of filtered hydrogen sulphid-water and the paste containing a small amount of free sulphur is ready for use; it is preserved in a desiccator filled with hydrogen. The yield is practically theoretical and the product of excellent quality.

Utilizing the hydriodic acid method of reduction as given by Whitely,¹ Biltz,² it is difficult to understand how the yields claimed could be obtained. Their directions were adhered to very strictly but the methods of maintaining the prescribed temperatures are certainly subject to question. Repeated trials failed to yield more than 30 per cent of theory, at the best, and in most cases, considerably less than that resulted. It was not until these methods were modified by the use of Dry Ice that yields in the neighborhood of 70 per cent were obtained. By the method essentially as Biltz³ prescribed for ethyluramil, the directions for carrying out the diphenylvioluric acid reduction are as follows:

The mortar and pestle to be used are packed in Dry Ice in a cardboard container for about fifteen minutes prior to use. Eighty-five cc. of hydriodic acid (spec. grav. 1.85) are placed in a large test tube and about 20 grams of lump-Dry Ice added. Twenty grams of diphenylvioluric acid are ground with about an equal amount of Dry Ice in the previously cooled mortar. The contents of the test tube are gradually added to the mortar with constant grinding. To the thick, brown mass of diphenyluramil and iodine, sufficient phosphoniumiodide to take up the free iodine is added and then 70% alcohol until solution is complete. The reaction mixture is transferred to a Dewar flask and maintained below 0°C. for twenty-four hours. Water is added and the material placed in a soda-lime desiccator (hydrogen filled). As the alcohol disappears, the colorless needles appear. Yield—between 65 and 70% of theory.

The titanous chloride method of reduction of uramil is accurate to the point of being quantitative, which neither of the other two methods is. On the other hand, although simple enough as an analytical method, it becomes rather unwieldy when attempts are made to put it on a large scale for preparative work. Unlike the other two reducing agents which, in themselves, are not particularly sensitive to air oxidation, this one is even more sensitive than the uramil itself—oxidizing instantly on exposure to air. This necessitates working in an atmosphere of hydrogen at

¹Stieglitz, Proc. Nat. Acad. of Sci. 9, 303 (1923).

²Whitely, J. Chem. Soc., 91, 1338 (1907).

³Biltz, Ann. 404, 204 (1914).

all times. The proper function of this method should be that of control on the others given.

The result of this study of methods of reduction of the substituted violuric acids, points clearly to a preference for the hydrogen sulphide from a standpoint of feasibility, ease of handling and yield.

PREPARATION OF THE MUREXIDES

The murexides as a class are rather easy to prepare if it is borne in mind that they are ammonium salts of exceedingly weak acids. These acids are weaker, as acids, than water and consequently hydrolize the more rapidly as the temperature and dilution are increased. All of these free acids have now been prepared by the writer which to the best of his knowledge has not been done before; neither has any mention been made of their existence. They are perfectly stable and will be described below.

In the preparation of the murexides, three general methods were used, namely, as an aqueous paste; as an aqueous solution of ammonium carbonate in contact with the solid uramil and aqueous alloxan; and in solution in 95 per cent alcohol.

Diphenylmurexide.—In this preparation, the diphenyluramil used was prepared by the hydrogen sulphide method as described above.

Ten grams of diphenyluramil is placed in a flask filled with hydrogen and 100 cc. of ammonium carbonate solution (18% aqueous solution) added to it. The mixture is shaken and warmed to 30° C. To this solution is added alloxan (13 gr.) dissolved in 50 cc. of water from which the oxygen has been removed by boiling. The deep purple (ammonium salt) diphenylmurexide begins to form around the solid uramil and soon a purple magma is formed.* This procedure is essentially analogous to that given by Tartar (1 Loc. Cit.) for methyl murexide.

In the preparation involving the paste, the operation is carried out precisely as above except that the flask is replaced by a stoppered bottle containing glass beads. This operation gives a better yield and quality than the above. No doubt, hydrolysis plays a large part in this difference. Where alcohol is used, the above amounts and conditions are adhered to. Here again, the yield and quality are better than in the first method.

Where it is desired to prepare the free acid of diphenylmurexide, a strong aqueous solution of the ammonium salt

*See graph and tables for unsubstituted alloxan.

is made up and the acid is precipitated with saturated sodium chloride solution. The free acid is a fiery cardinal precipitate, practically insoluble in water, soluble in alcohol. On the other hand, if potassium chloride is used in place of the sodium, the ammonium salt will be salted out, of a bluer-red and soluble in water. This difference is due to the fact that potassium chloride is practically neutral, that is, has the same p_H as water, whereas sodium chloride is probably sufficiently lower in p_H to liberate the free acid and still not sufficiently acid to decompose the molecule at the amino bridge.

The di-tolyls and di-naphthyls all show this same point of the differentiation between the ammonium salt and the free acid of the murexide with respect to sodium and potassium chloride. These latter free acids have been prepared only in relatively small amounts and until sufficient amounts are available thoroughly to check weights, reactions and general properties, it would be rash to make any claim.

Acid Decomposition. Diphenylmurexide (9 g.) was dissolved in 30 cc. of water and hydrochloric acid (conc.) added to the solution till colorless and acid to litmus; the solution was then brought back to faint alkalinity with caustic soda. The washed, dried powder obtained gave no definite absorption band in saturated solution. From the filtrate, crystals (3.6 g.) were obtained which when dissolved in 10 cc. of water and repeatedly haviged in concentration, gave the data which, when plotted and tabulated, coincide approximately with alloxan. The melting point uncorrected was 155 C., somewhat below the true value for alloxan.

Whereas, in the previous work it was shown that on acid hydrolysis the diphenylmurexide (as made from diphenyluramil and unsubstituted alloxan) gave diphenyluramil and unsubstituted alloxan, the work of this particular portion was designed to test this principle by cross-condensing and subsequently hydrolizing the diphenylmurexide (as made from diphenylalloxan and unsubstituted uramil), to determine on which side of the nitrogen-bridge the split occurs. If the diphenylalloxan and uramil are regenerated by hydrolysis, then the evidence for the existence of the two tautomers of the unsymmetrical diphenylmurexide can be demonstrated by optical means and the Stieglitz theory proved.

The first step in this work consisted in the preparation of diphenylalloxan. This has been done in two general ways, as follows:

- (1) Separation and purification of the hydrolysis mixture from the hydrolysis of tetraphenyl murexide. The latter is prepared (a) by allowing diphenyluramil to oxidize and condense, spontaneously, in the air, or, (b) by chemically oxidizing the same compound, neutral.
- (2) By the direct oxidation of the diphenyluramil on the acid side.

The requirements of Number 2 preclude all methods of oxidation of the diphenyluramil, neutral or on the alkaline side, owing to the fact that the instant any diphenylalloxan is formed it condenses spontaneously with some of the unchanged diphenyluramil to produce tetraphenyl murexide. Accordingly, methods had to be devised for the acid oxidation of this substance and this proved to be a problem in which considerable difficulty was encountered.

The next step after obtaining the diphenylalloxan consisted in condensing the latter with unsubstituted uramil with the subsequent hydrolysis of the murexide thus produced.

Diphenylalloxan.--Owing to the fact that the oxidation of diphenyluramil cannot be carried out in neutral or alkaline solution without the formation of tetraphenylmurexide, only acid oxidizing agents were considered. All of the usual agents, such as chlorine, nitric acid, acid-dichromate, acid-permanganate, and lead peroxide in acetic, sulphuric and hydrochloric acids were used. Neither the nitric nor chlorine methods gave pure products; the melting points extended over a large range, due no doubt, to nitration and chlorination. In each case where the oxidizing agent contained a metal ion such as chromium, manganese, lead or iron, etc., an intensely colored lake resulted. When these trials failed, an attempt was made to find out if this substance could be air oxidized in faintly acid media, it was partly by accident that it was discovered that it could be done. It was noticed that when weakly acid solutions of diphenyluramil sulphate were allowed to stand exposed to the air for about a day, pearly white foam begins to collect on the surface. When this occurs, if the flask be vigorously shaken in the air, for about twenty minutes, this pearly mass fills the flask. Analysis showed this substance to be diphenylalloxan. Because of the great sensitiveness of uramil to air-oxidation in neutral and alkaline solution, it isn't strange that this property should carry over to the acid side. Also, as was expected, it was found that the stronger the acid, the slower

the oxidation; that at 45 per cent strength of sulphuric acid this aryl uramil could be preserved for some time but in weak acid the reaction is quite rapid. The procedure is best carried out as follows:

The diphenyluramil hydrosulphide solution after freeing of sulphur, is gradually acidified with cold, dilute sulphuric acid of 5% strength until the crystals begin to throw out. At this point the solution is allowed to stand in the air for about twenty-four hours, at the end of which time the solution is completely acidified and vigorously shaken if the crystals fail to form immediately. The ease or difficulty of causing crystallization at this point depends on which one of the hydrates of diphenylalloxan is present. The keto-form is insoluble; the monohydrate, slightly soluble and the higher hydrate is very soluble. Boiling or even heating to any extent, seems to convert the hydrates or the ketone into diphenylalloxantine, which is insoluble. Crystals of the polyhydrate of approximately four inches in length have been obtained from the acid mother-liquor from the above preparation by slow, cold evaporation in a desiccator. Crystals of exact snow-shoe shape, of the monohydrate have been obtained from these same mother-liquors under similar conditions. The ketone is probably formed under conditions quite similar to those necessary for the alloxantine.

Diphenylalloxan prepared as above condenses with unsubstituted uramil either with anhydrous ammonia in benzol or with 28 per cent ammonium carbonate aqueous solution to form diphenyl murexide. Diphenylalloxantine, however, does not condense under these conditions. In the table of analytical data given below, it will be seen that both diphenylalloxantine and diphenylalloxan (keto-form) are given as fulfilling the requirements of these data. The evidence favoring the alloxantine alternative as better fitting these data is as follows:

1. Melting sharply, without decomposition, at elevated temperature indicates greater stability which would be expected of the carbon-carbon union of alloxantine rather than the ketone.

2. Diphenylalloxan hydrate, on drying, would be expected to go over to the ketone with loss of molecule of water; this substance becomes plastic at 110° C. indicating some change such as loss of water. As this plastic material is raised in temperature it turns red and melts definitely between 171° and 175° C. The ketone form might be expected to exhibit these characteristics; diphenylalloxantine, on the other hand, shows no change whatsoever until it reaches the melting point. Thus, this substance behaves like alloxan hydrate.

3. The hydrated form of diphenylalloxan condenses readily with uramil, whereas the questionable one does not. There is no good reason why the ketone should not, therefore, it is probably the alloxantine form and not the ketone form.

Compound	Melting Point	Nitrogen		Carbon	
		Theoret.	Actual	Theoret.	Actual
Diphenylurea.....	236° C.	13.20	13.16	75.35	75.12
Diphenylbarbituric acid	228° C.	10.00	9.82	68.05	67.88
Diphenylvioluric acid..		14.03	13.75	61.93	61.34
Diphenyluramil.....		14.23	14.09	65.10	64.28
Diphenylalloxan (keto))	202° C.	9.52	9.54	65.10	65.36
Diphenylalloxantine...)	202° C.	9.52	9.54	65.10	65.36
Diphenylalloxan..... (hydrate)	171-175° C. Dec. turns red and plastic 108°	9.10	9.00	61.93	61.66

INTERPRETATION OF RESULTS

1. The data for each individual murexide are so tabulated as to show the angle of extinction and $\tan^2$ for each corresponding wave-length.

2. The percentages of absorption are calculated from the data and plotted against the wave-length in the graphs; the absorption maximum being shown in each case at unit concentration.

3. The graph obtained from the data for the product obtained from acid decomposition of diphenylmurexide shows approximate co-incidence of the absorption maximum with that of unsubstituted alloxan.

4. Absolute verification of coincidence here can mean only one thing, namely, the substantiation of the Stieglitz view as based on the points outline on page 1.

5. This absolute verification was obtained by augmenting this work of photographing the absorption bands of alloxan, diphenylalloxan, uramil and diphenyluramil—all in the ultraviolet. This can be further confirmed by parallelling the same work with the naphthyl derivatives.

Notes, remarks.—Alloxan (prepared from uric acid, probably the keto-form) shows no reaction or color change with sodium nitrite solution; it remains insoluble as it is in water.

- (2-b) Diphenylalloxan (from hot aqueous sulphuric acid solution), shows no reaction or solubility in sodium nitrite solution. Probably the keto-form.
- (3-c) Diphenylalloxan (polyhydrate) (from gradual concentration of sulphuric acid solution) (filtrate from hydro-sulphide reduction), shows neither reaction nor color change with sodium nitrite solution. Very soluble in water, re-crystallizes in long, beautiful needles.
- (4-d) Diphenylalloxan (monohydrate) (from air oxidation of dilute acid solution (filtrate from hydro-sulphide reaction)), shows neither reduction nor color change with sodium nitrite solution. Fairly soluble in water.
- (5) Diphenylbarbituric acid soluble in boiling water.
 " " " " in hot benzol.
 " " " " in cold, dilute,
 caustic solutions.
 " " precipitates from caustic solu-
 tions with acid.
- (6) Diphenylvioluric acid (sodium salt) turns colorless and throws down a precipitate when treated with caustic. Under certain conditions of preparation of this sodium violurate, this same bleaching effect occurs when either the mole proportion of sodium nitrite is too great or when the temperature is too high. In addition to the above changes, a gas is evolved (carbamine odour) indicating hydrolysis. This is undoubtedly brought about because of the excess of a weak salt in too dilute and too hot a solution, liberating large numbers of hydroxyl ions to which the sodium violurate is very sensitive. When carried out in a moderate sized preparation, about two-thirds of the yield can be converted into this colorless, very soluble salt. By partial salting out, the colored salt is first thrown out and the colorless salt can be precipitated from the faintly colored filtrate by the addition of more salt. Nitrogen determinations show 9.52 per cent, indicating the loss of one nitrogen atom from the molecule.

SUMMARY

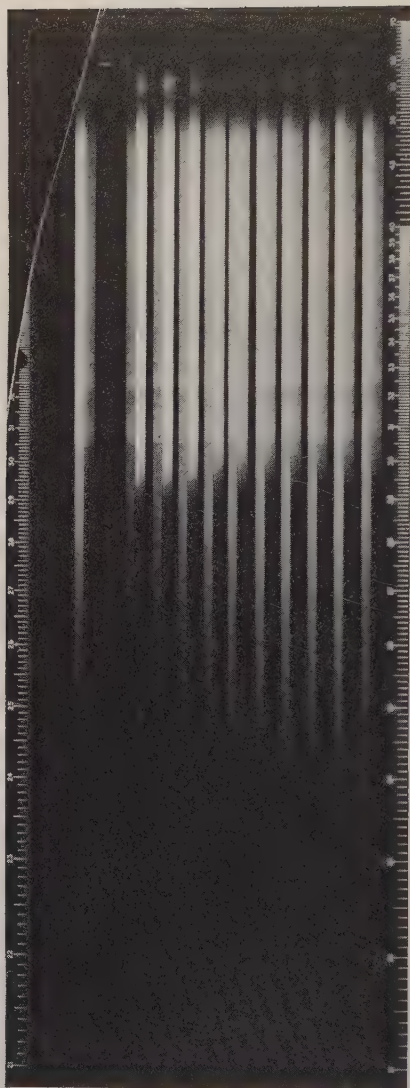
In order to check the criteria as covered by the several points given in the Introduction, it was necessary to study optically a variety of compounds; this was done by means of the spectroscope, both in the visible and in the ultra-violet regions. Also, it was necessary to prepare a number of important compounds as given in this paper, in order that this optical study might be carried out. Most of the preparative work involved the successive steps necessary to attain the compounds directly involved in the proof of the problem. The preliminary proof is to be found in the graphs showing the absorption maxima, particularly, of the diphenylmurexide hydrolysis products and alloxan. The murexide

was made from alloxan and diphenyluramil and the graph showed the presence of alloxan in the hydrolysis product. Thus the murexide split into the two identical products from which it was made and having exhibited all the properties of a dyestuff while in the murexide form, the color production must have been independent of the shifting of groups during that color state. Had the said groups shifted, then, a corresponding migration of electrons would have been necessary, concomitantly. Conversely, inasmuch as the groups did not shift, neither could the electrons have migrated unless the entire basis of the accepted theory of electronics is to be abandoned. Extending the above proof into the ultra-violet, bands were photographed in the hope of not only confirming the above but of bringing forth evidence of the existence of two tautomeric forms of the unsymmetrical diphenylmurexide. This murexide was prepared, on the one hand, from diphenyluramil and alloxan and, on the other, from diphenylalloxan and uramil. The hydrolysis products in each case were photographed in the spectrograph and the plates compared with plates similarly made from the pure individual components used in making up the murexides. The results are recorded in the prints on pages twenty-two and three, and show that the a-tautomer of diphenylmurexide as made from diphenyluramil and alloxan gave these same two components on hydrolysis and that the b-tautomer of the diphenylmurexide as made from diphenylalloxan and uramil, likewise, gave the latter two components on hydrolysis. The alloxans were used for identification in each case because of the greater stability and freedom from tendency to color and also because of the greater convenience of washing away the soluble uramil and diphenyluramil as the hydrochlorides; thus, in the first case the hydrolysis component showed an absorption band beginning at 2,900 to 3,000 Angstroms which corresponds with the plate from the pure alloxan from which the murexide was made. In the second set, the hydrolysis component showed an absorption band beginning at 3,300 to 3,400 Angstroms which corresponds with the plate from the pure diphenylalloxan from which the other tautomeric murexide was made.

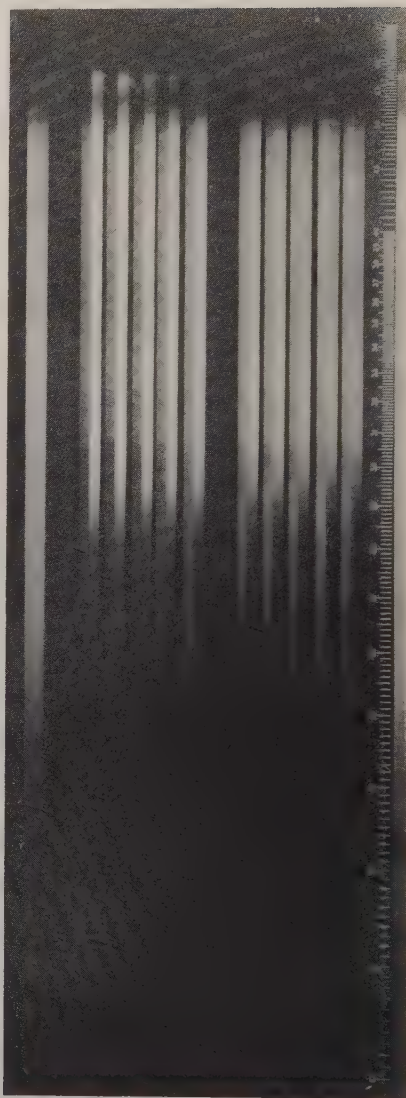
CONCLUSION

In conclusion, it may be said that the Stieglitz theory of color is further confirmed by the results obtained in the work described in this paper, that is, the results as they transpired were predictable by the theory.

PLATE I

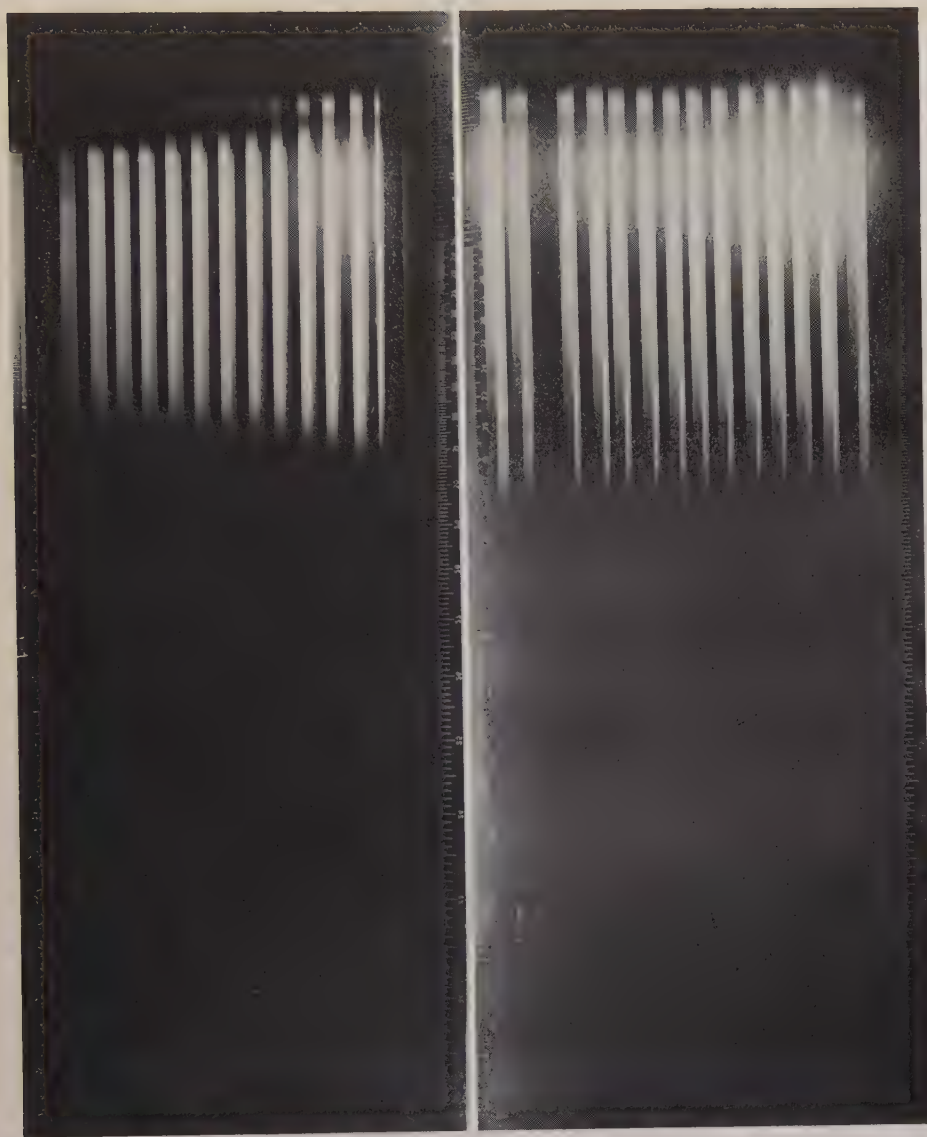


Alloxan
w.-l. 2900 - 3000 Å



Diphenylmurexide (Hydrolyzed)
w.-l. 2900 - 3000 Å

PLATE II



Diphenylalloxan
w. - 1. 3300 - 3400 Å

B- Diphenylmurexide (Hydrolyzed)
w. - 1. 3300 - 3400 Å

ABSORPTION SPECTRA
UNSUBSTITUTED MUREXIDE

Parts Per Million	160 p.p.m.		80 p.p.m.		40 p.p.m.		20 p.p.m.		10 p.p.m.	
Wavelength	θ	$\tan^2\theta$	θ	$\tan^2\theta$	θ	$\tan^2\theta$	θ	$\tan^2\theta$	θ	$\tan^2\theta$
7,000	57	.423	58	.390	57	.423	56.5	.438	48	.810
6,800	57	.423	58	.390	57	.423	56.5	.438	48	.810
6,600	60	.334	58	.390	60	.390	58	.390	56	.474
6,400	73	.093	62	.283	66	.198	49	.755	54	.527
6,200	86	.0048	78	.045	74	.082	48	.810	53	.567
6,000	90	.000	86	.004	82	.019	41	.931	51	.655
5,800	90	.000	90	.000	86	.004	49	.755	54	.527
5,600	90	.000	90	.000	90	.000	80	.031	78	.045
5,400	90	.000	90	.000	90	.000	90	.000	88	.001
5,200	90	.000	90	.000	90	.000	80	.031	82	.019
5,000	80	.000	86	.004	83	.015	60	.333	54	.527
4,800	89	.000	80	.031	76	.062	52	.610	51	.655
4,600	82	.019	64	.237	52	.610	48	.810	46	.932
4,400	84	.011	75	.071	50	.704	46	.932	70	.132
4,200	84	.011	78	.045	48	.810	60	.333	88	.001
4,000	82	.019	80	.031	46	.932	70	.132	90	.000

ABSORPTION SPECTRA
DI-PHENYL-VIOLURIC ACID
(Sodium salt)

Parts Per Million	160 p.p.m.		80 p.p.m.		40 p.p.m.		20 p.p.m.		10 p.p.m.	
Wavelength	θ	$\tan^2\theta$	θ	$\tan^2\theta$	θ	$\tan^2\theta$	θ	$\tan^2\theta$	θ	$\tan^2\theta$
7,000	70	.132	66	.198	74	.082	82	.019	84	.011
6,800	72	.105	68	.163	72	.105	73	.093	86	.004
6,600	76	.062	68	.163	73	.093	73	.093	84	.011
6,400	80	.031	64	.237	70	.132	72	.105	80	.031
6,200	86	.004	62	.282	62	.292	68	.163	76	.062
6,000	88	.001	68	.168	66	.198	52	.610	68	.163
5,900	90	.000	72	.105	68	.168	70	.132	53	.610
5,800	90	.000	80	.031	78	.045	82	.019	78	.045
5,700	90	.000	88	.001	88	.001	89	.000	88	.001
5,600	90	.000	90	.000	90	.000	87	.002	76	.062
5,500	90	.000	90	.000	86	.004	78	.045	68	.163
5,400	90	.000	90	.000	84	.011	76	.062	70	.132
5,300	89	.000	88	.001	80	.031	72	.105	71	.118
5,200	88	.001	80	.031	78	.045	70	.132	72	.105
5,100	87	.002	74	.082	74	.082	68	.163	74	.082
5,000	86	.004	74	.082	74	.082	69	.147	78	.045
4,800	84	.011	74	.082	74	.082	72	.105	80	.031
4,600	80	.031	76	.062	76	.082	76	.082	84	.011
4,400	79	.147	78	.045	78	.045	80	.031	86	.004
4,200	78	.045	80	.031	80	.031	84	.011	86	.004
4,000	78	.045	80	.031	82	.019	84	.011	86	.004

UNSUBSTITUTED MUREXIDE

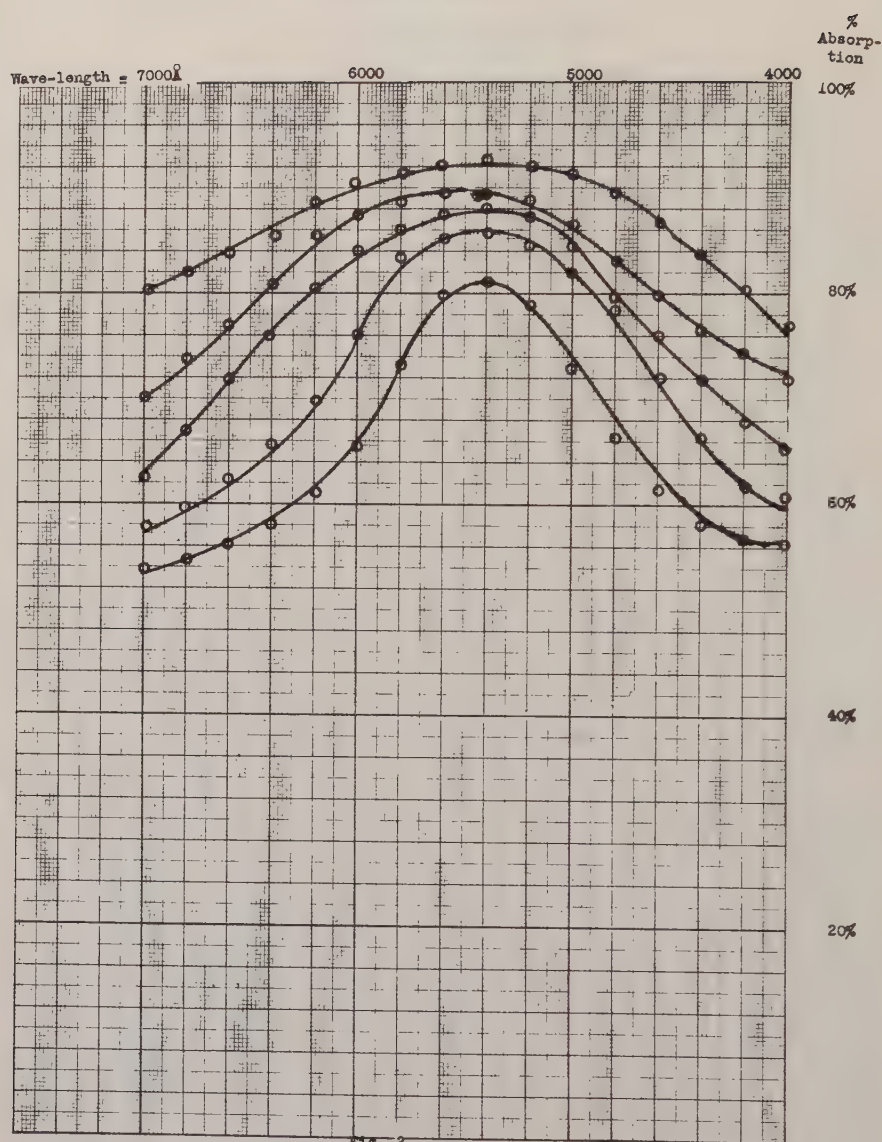


Fig. 2

DI-PHENYL-VIOLURIC ACID

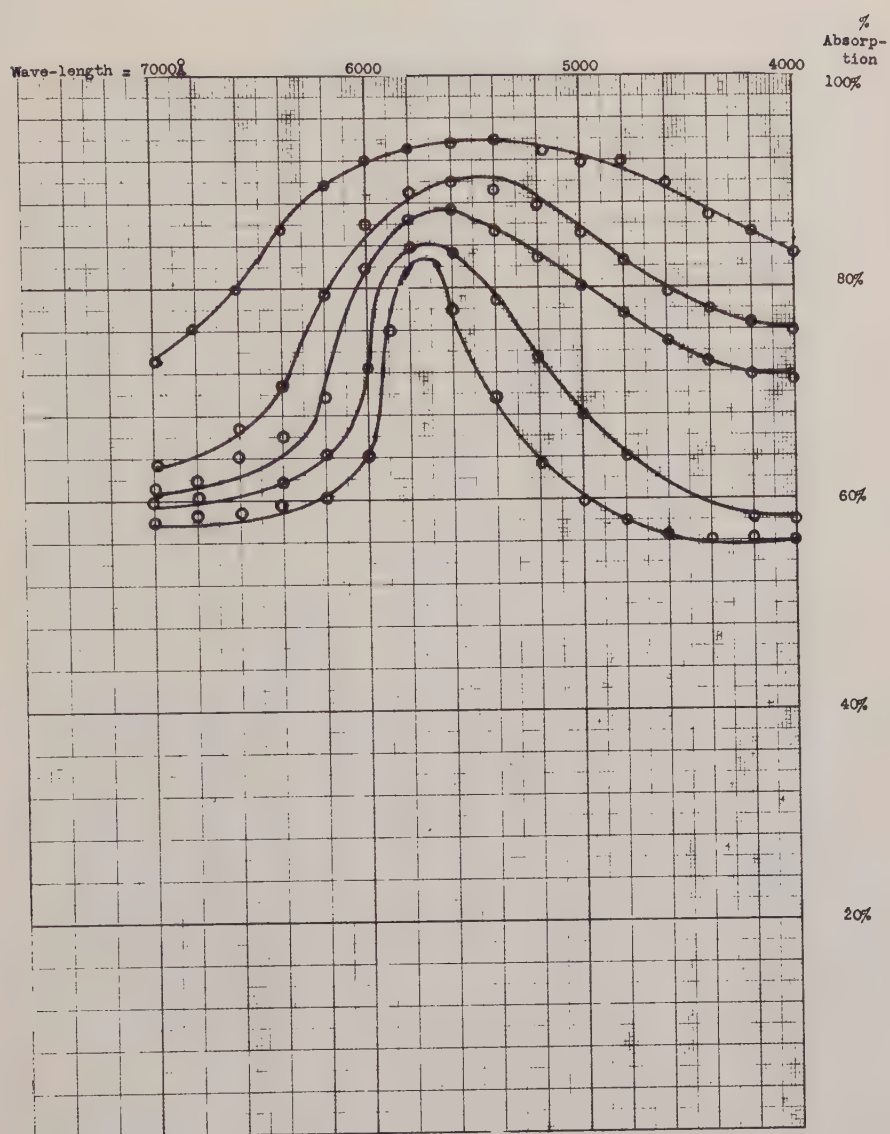


Fig. 3

ABSORPTION SPECTRA

DI-PHENYL MUREXIDE

Parts Per Million	160 p.p.m.		80 p.p.m.		40 p.p.m.		20 p.p.m.		10 p.p.m.	
Wavelength	θ	$\tan^2 \theta$	θ	$\tan^2 \theta$	θ	$\tan^2 \theta$	θ	$\tan^2 \theta$	θ	$\tan^2 \theta$
7,000	68	.163	64	.237	66	.198	72	.105	81	.025
6,800	64	.237	62	.282	68	.163	70	.132	80	.031
6,600	76	.062	60	.333	64	.237	60	.333	76	.062
6,400	80	.031	68	.163	68	.163	56	.454	58	.390
6,200	86	.004	74	.082	70	.132	60	.333	54	.527
6,000	90	.000	78	.045	76	.062	62	.282	52	.610
5,900	90	.000	84	.011	80	.031	74	.082	48	.810
5,800	90	.000	86	.004	86	.004	84	.011	46	.932
5,700	90	.000	90	.000	90	.000	86	.004	74	.082
5,600	90	.000	90	.000	90	.000	90	.000	52	.610
5,500	90	.000	90	.000	90	.000	90	.000	48	.810
5,400	90	.000	90	.000	90	.000	90	.000	47	.869
5,300	90	.000	89	.000	86	.004	80	.031	46	.932
5,200	90	.000	78	.045	79	.147	62	.282	45	1.000
5,100	89	.000	85	.007	76	.062	61	.307	45	1.000
5,000	88	.001	82	.019	75	.071	59	.361	48	.810
4,800	86	.004	80	.031	62	.282	46	.932	50	.704
4,600	87	.002	72	.105	58	.390	47	.869	62	.282
4,400	86	.004	70	.132	56	.454	54	.527	72	.105
4,200	84	.011	68	.163	54	.527	62	.282	76	.062
4,000	82	.019	66	.198	51	.655	83	.015	86	.004

ABSORPTION SPECTRA
TETRA-PHENYL MUREXIDE

Parts Per Million	160 p.p.m.		80 p.p.m.		40 p.p.m.		20 p.p.m.		10 p.p.m.	
Wavelength	θ	$\tan^2\theta$	θ	$\tan^2\theta$	θ	$\tan^2\theta$	θ	$\tan^2\theta$	θ	$\tan^2\theta$
7,000	56	.454	55	.490	52	.610	46	.932	82	.019
6,800	56	.454	55	.490	54	.527	46	.932	83	.015
6,600	58	.390	57	.421	58	.391	46	.932	80	.031
6,400	66	.198	64	.237	70	.132	48	.810	82	.019
6,200	80	.031	74	.082	76	.062	64	.237	54	.527
6,000	90	.000	88	.001	82	.019	80	.031	56	.454
5,900	90	.000	90	.000	86	.004	84	.011	88	.001
5,800	90	.000	90	.000	90	.000	89	.000	66	.198
5,700	90	.000	90	.000	89	.000	88	.001	64	.287
5,600	90	.000	90	.000	89	.000	82	.019	46	.932
5,500	89	.000	88	.0001	80	.031	64	.237	45	1.000
5,400	87	.002	86	.004	76	.062	60	.333	48	.810
5,300	84	.011	82	.019	70	.132	60	.333	52	.610
5,200	80	.031	78	.045	72	.105	64	.237	56	.454
5,100	78	.045	77	.053	74	.082	66	.198	60	.333
5,000	76	.062	76	.062	76	.062	68	.163	68	.163
4,800	74	.082	73	.093	78	.045	70	.132	72	.105
4,600	74	.082	73	.093	80	.031	72	.105	74	.082
4,400	72	.105	71	.118	82	.019	76	.062	78	.045
4,200	70	.132	69	.147	84	.011	86	.004	84	.011
4,000	68	.163	68	.163	86	.004	88	.001	87	.001

DI-PHENYL MUREXIDE

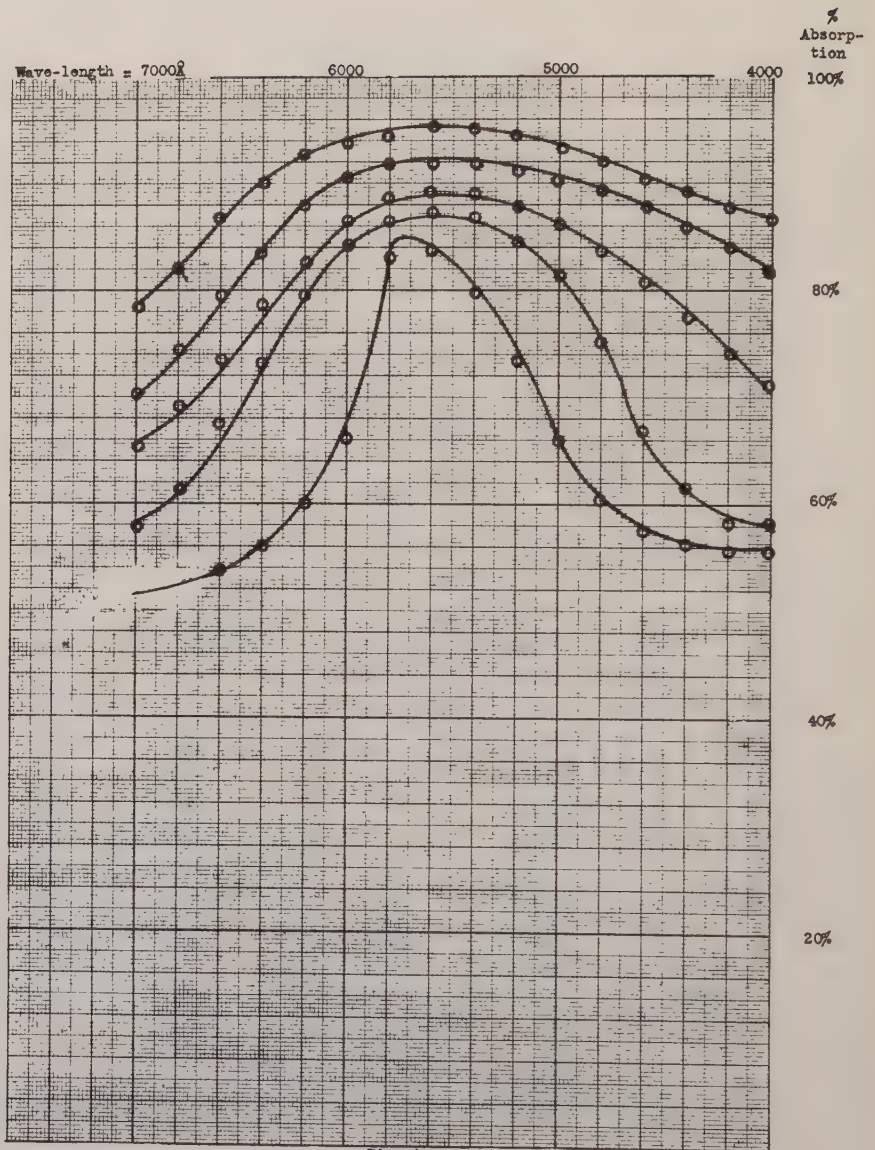


Fig. 4

TETRA-PHENYL MUREXIDE

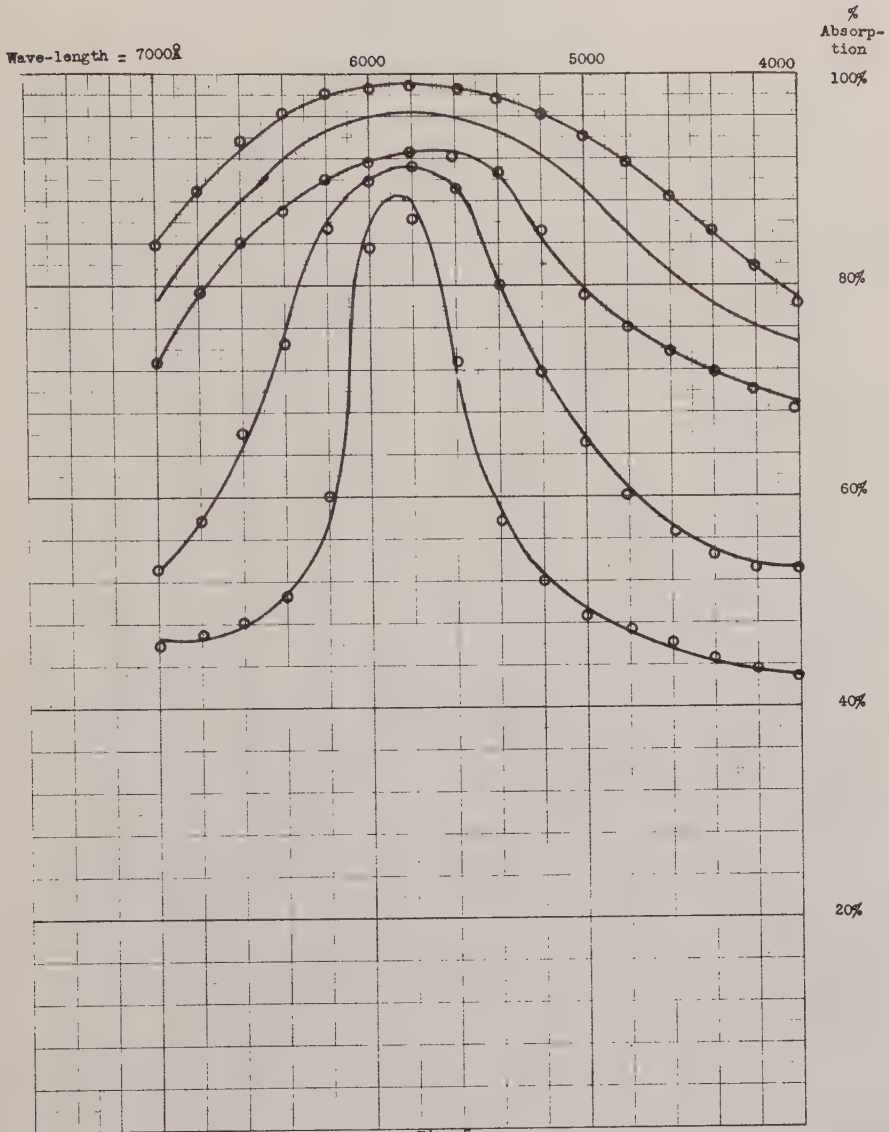


Fig. 5

ABSORPTION SPECTRA
UNSUBSTITUTED ALLOXAN

Parts Per Million	250,000 p.p.m.		125,000 p.p.m.		62,500 p.p.m.		31,250 p.p.m.		15,625 p.p.m.	
Wavelength	θ	$\tan^2 \theta$	θ	$\tan^2 \theta$	θ	$\tan^2 \theta$	θ	$\tan^2 \theta$	θ	$\tan^2 \theta$
7,000	76	.062	70	.132	64	.237	78	.045	80	.031
6,800	77	.053	72	.105	62	.282	80	.031	79	.037
6,600	78	.045	74	.082	63	.259	79	.037	78	.045
6,400	80	.031	75	.071	65	.217	76	.062	77	.058
6,200	84	.011	80	.031	72	.105	74	.082	76	.062
6,000	88	.001	84	.011	76	.062	73	.093	75	.071
5,900	89	.000	86	.004	78	.045	72	.105	74	.082
5,800	90	.000	87	.002	80	.031	71	.118	73	.093
5,700	90	.000	88	.001	81	.025	71	.118	72	.105
5,600	90	.000	88	.001	82	.019	72	.105	71	.093
5,500	90	.000	88	.001	84	.011	73	.093	70	.132
5,400	90	.000	89	.000	86	.004	74	.082	69	.147
5,300	90	.000	89	.000	87	.003	75	.071	68	.163
5,200	90	.000	90	.000	89	.000	77	.053	67	.180
5,100	90	.000	90	.000	90	.000	80	.031	66	.198
5,000	90	.000	90	.000	90	.000	88	.002	65	.217
4,800	90	.000	90	.000	90	.000	90	.000	78	.045
4,600	89	.000	86	.004	82	.019	90	.000	82	.019
4,400	86	.004	82	.019	78	.045	77	.053	62	.282
4,200	84	.011	80	.031	66	.198	68	.163	60	.333
4,000	82	.019	56	.454	64	.237	56	.454	66	.198

ABSORPTION SPECTRA
HYDROLYZED DIPHENYL MUREXIDE

Parts Per Million	250,000 p.p.m.		125,000 p.p.m.		62,500 p.p.m.		31,250 p.p.m.		15,625 p.p.m.	
Wavelength	θ	$\tan^2\theta$	θ	$\tan^2\theta$	θ	$\tan^2\theta$	θ	$\tan^2\theta$	θ	$\tan^2\theta$
7,000	77	.062	71	.119	66	.198	76	.062	77	.058
6,800	79	.087	70	.132	63	.259	78	.045	78	.045
6,600	81	.025	74	.082	62	.282	79	.037	77	.058
6,400	83	.015	77	.062	63	.259	78	.045	77	.058
6,200	85	.007	82	.019	69	.147	74	.082	76	.062
6,000	89	.000	85	.007	76	.062	73	.093	76	.062
5,900	90	.000	86	.004	77	.053	72	.105	74	.082
5,800	90	.000	87	.002	80	.031	72	.105	73	.098
5,700	90	.000	89	.000	86	.004	73	.098	73	.093
5,600	90	.000	89	.000	86	.004	73	.093	72	.105
5,500	90	.000	88	.001	84	.011	72	.105	71	.118
5,400	90	.000	89	.000	86	.004	75	.071	70	.132
5,300	90	.000	89	.000	87	.003	75	.071	70	.132
5,200	90	.000	90	.000	88	.001	76	.062	68	.168
5,100	90	.000	90	.000	89	.000	82	.019	67	.180
5,000	90	.000	89	.000	88	.001	84	.011	66	.198
4,800	90	.000	89	.000	88	.001	87	.003	74	.082
4,600	88	.001	88	.001	88	.001	87	.003	80	.031
4,400	87	.003	84	.011	79	.037	78	.045	78	.045
4,200	86	.004	82	.019	72	.105	74	.082	70	.132
4,000	84	.011	68	.163	66	.198	60	.333	68	.168

UNSUBSTITUTED ALLOXAN

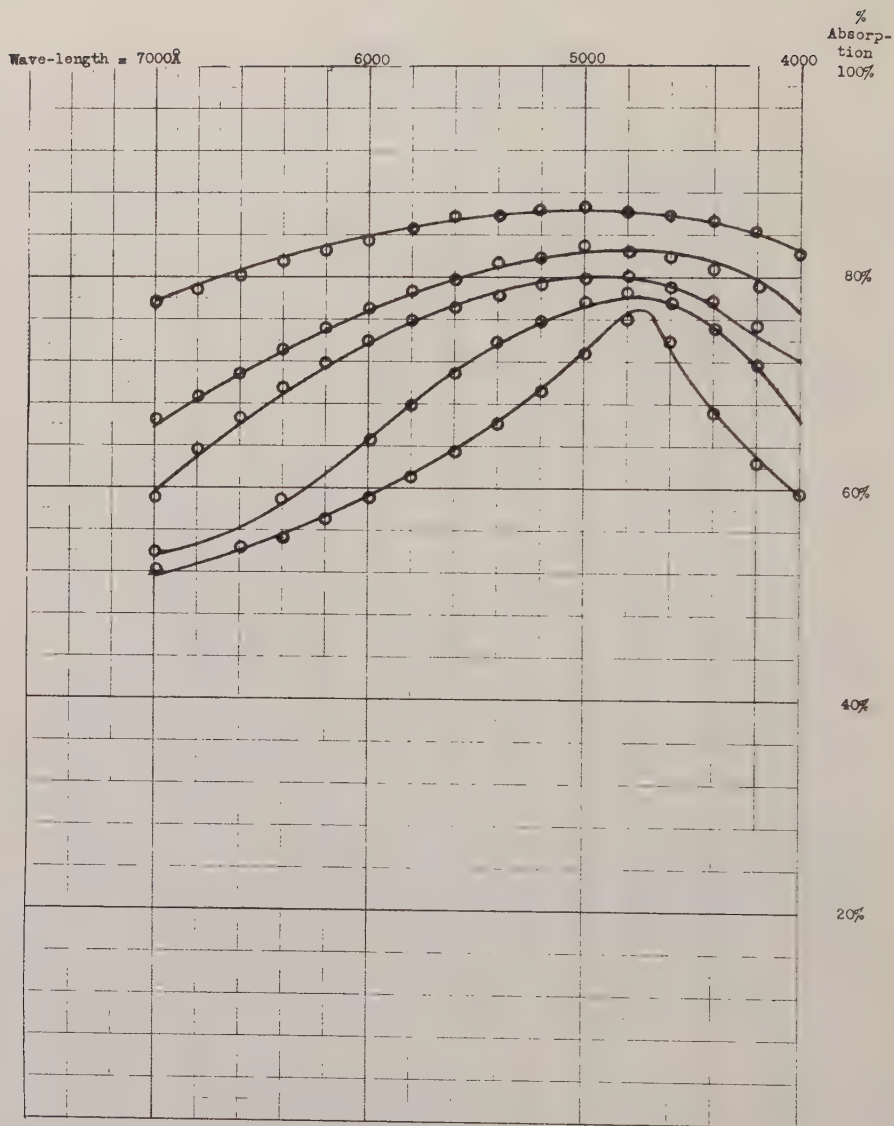


Fig. 6

HYDROLYZED DIPHENYL MUREXIDE

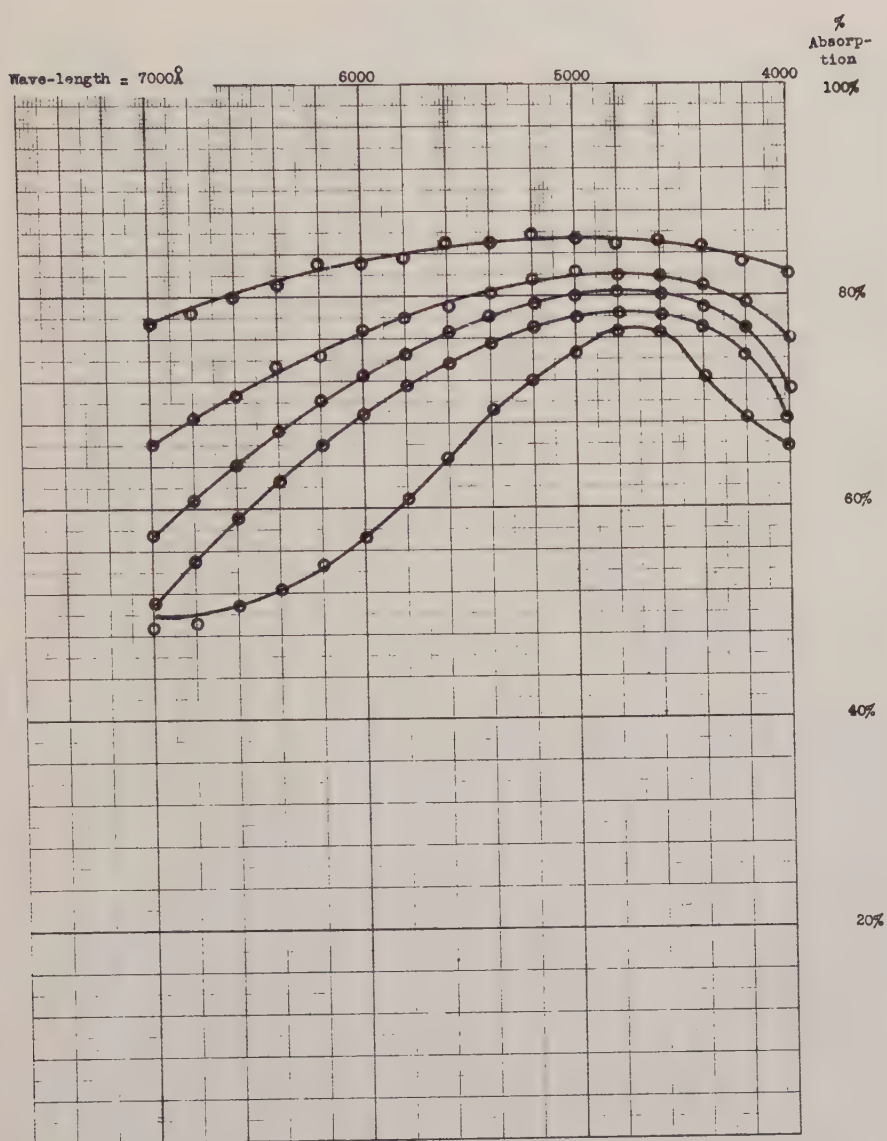


Fig. 7

Unsubstituted Alloxan
and
Hydrolysed Diphenylmurexide

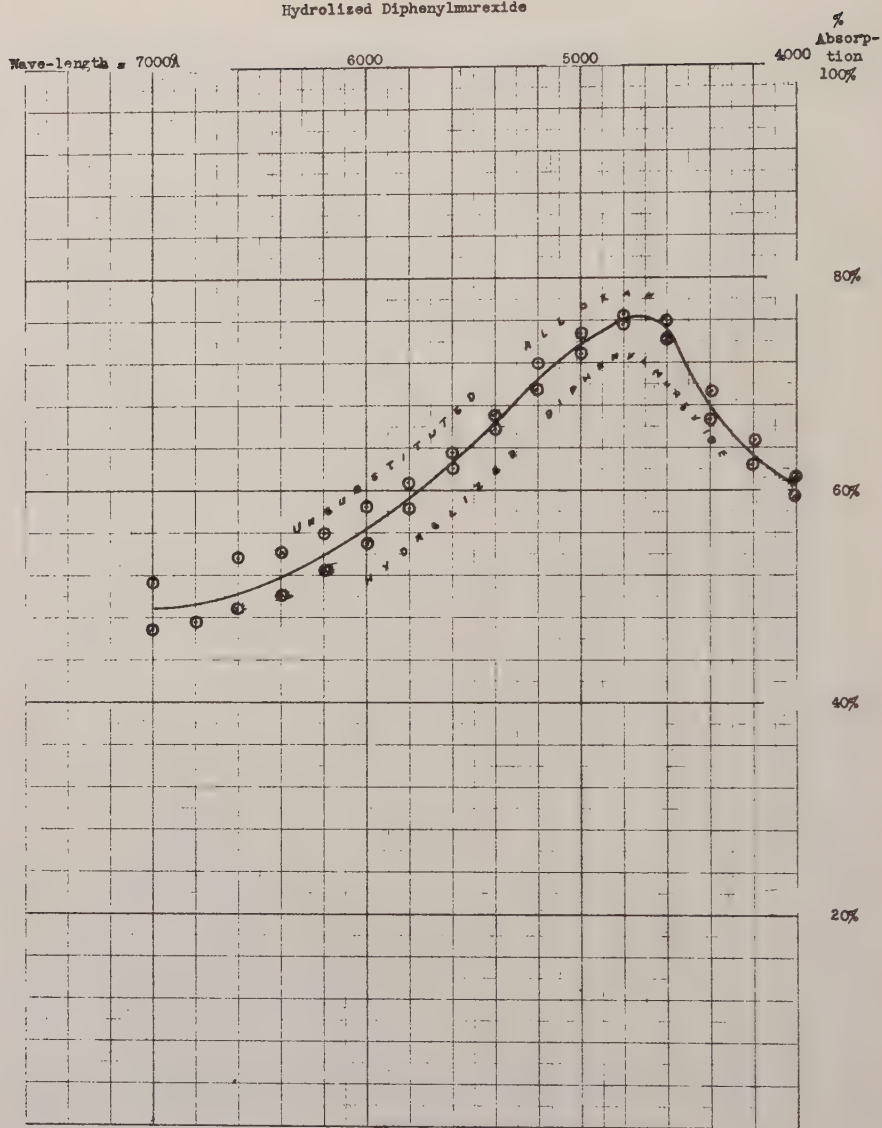
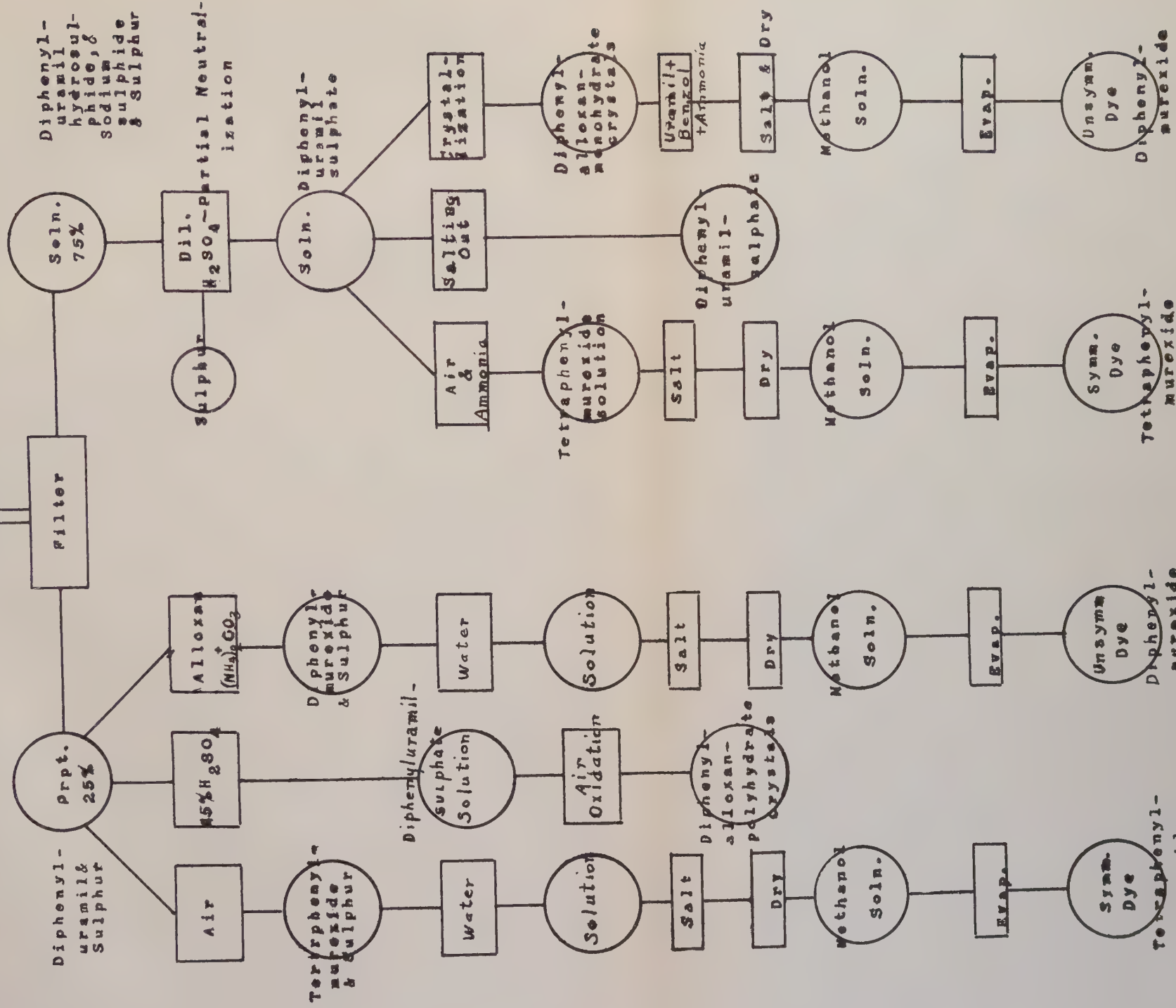


Fig. 8

DIAGRAMMATIC SCHEME

Diphenyluramil Hydrosulphide Solution



α-tautomer

β-tautomer

